Dynamic Response of Simple Liquids from Vibration-Transit Theory

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The Vibration-Transit (V-T) theory for liquid dynamics [1], recently developed in our group, is a new fundamental tool to evaluate accurate equations of state but also it gives a new insight in the physics of liquids. In this work we applied V-T theory to study the dynamic response of a simple liquid. We found not only support for the theory, through comparison with molecular dynamics (MD) simulation, but also we were able to contribute to the understanding of the microscopic origin of the Brillouin peak of inelastic scattering experiments.

Vibration-Transit theory is based on the idea that the many-body potential energy surface underlying the motion of the liquid system consists of an enormous number of valleys, the overwhelming majority of which correspond to random configurations of the atoms in the system. All these random valleys have the same energy and the same macroscopic properties. The barriers between valleys are sharp and the time spent by the system in the transitions from one valley to another is almost instantaneous.

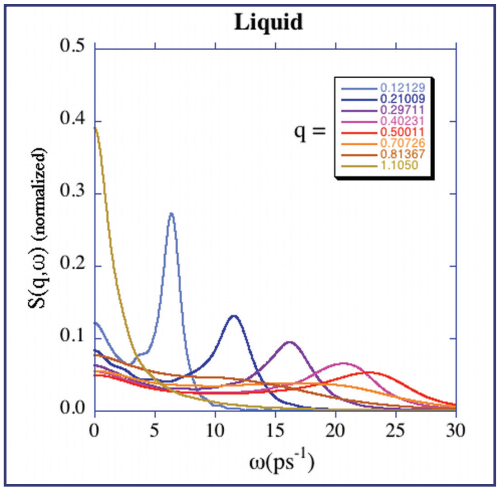


Figure 1—
Dynamic Structure Factor for sodium at T = 395K from molecular dynamics simulation for eight different values of q (in units of bohr^{-1}). In this case the system wanders among many different random valleys; there is ample diffusion.

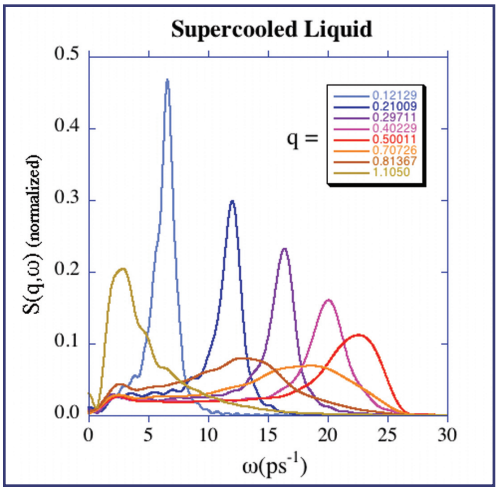
The random valleys are quasiharmonic and they all have the same distribution of normal mode frequencies. The entire motion in the monatomic liquid is then comprised of two elements: vibrations in the random valleys and transits between them. Both experimental results and MD simulations support this view.

One interesting probe of the dynamic response of liquids is the dynamical structure factor, S(q, ω), which is the power spectrum of the time dependent density-density correlation function, and therefore a direct test of the microscopic dynamics. On the other hand S(q, ω) enters in an explicit formula for the cross sections in inelastic scattering experiments and can therefore be actually measured.

A typical behavior of S(q, ω) from MD simulation is shown in Fig. 1. Our system is a simple monatomic liquid, sodium at the density of the melt, with 500 particles with periodic boundary conditions, at a temperature just above melting, T = 395K. We explore a range of small q, close and up to the maximum of S(q), the static structure factor. The Brillouin peak is clearly dominant. As q increases, its maximum shifts from small ω to larger ones and eventually it turns around. At q = 1.1050 bohr^{-1}, almost at the maximum of S(q), the Brillouin peak disappears, while the Rayleigh peak becomes dominant.

If the liquid is rapidly quenched, it falls in one of the random valleys and a low temperature trajectory remains trapped inside that valley for a very long time. S(q, ω) in this supercooled liquid, shown in Fig. 2, exhibits a very similar behavior to the liquid, but the Rayleigh peak has disappeared and the Brillouin peak is sharper.

For this supercooled liquid, V-T theory gives an explicit expression for S(q, ω) in terms of only the positions of the atoms in a random configuration (at the bottom of the valley) and its normal mode frequencies and eigenvectors (there are no transits). A comparison of the V-T theory prediction and MD evaluation for one typical q is shown in Fig. 3. The agreement is perfect, showing that the approximations used in the theory (harmonic one-phonon) are highly accurate.



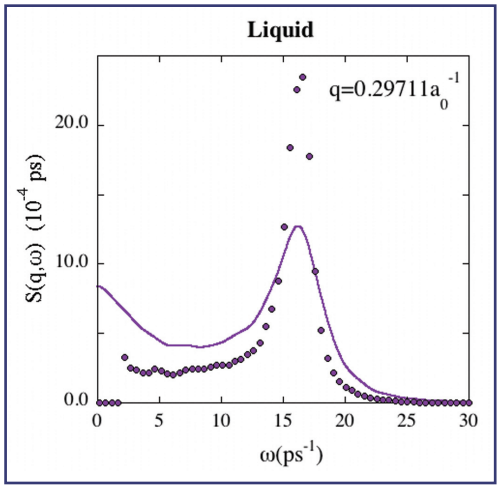
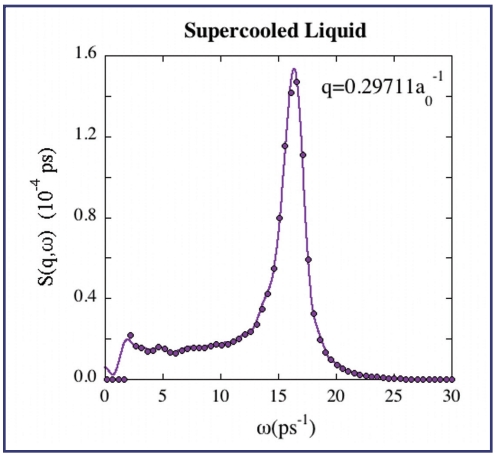


Figure 2—
As in Fig. 1, but at T = 24K. In this case the system is trapped in a single random valley; there is no diffusion.

Figure 3—
Comparison between molecular dynamics and V-T theory for one of the cases shown in Fig. 2 at T = 24K.

But furthermore we learned an important fact about the nature of the Brillouin peak. From the theory, S(q, ω) is the sum of statistically independent cross sections for a set of noninteracting vibrational modes. This means that the width of the Brillouin peak in Fig. 2 and Fig. 3 is the *natural width*. No relaxation process is involved.

whole range of q for which a Brillouin peak is present, as depicted in Fig. 5. The figure proves that this dispersion curve for the liquid (which is in agreement also with experiments) can be completely evaluated from only the independent vibrational modes in a single valley, without the need to invoke coupling between the modes and relaxation



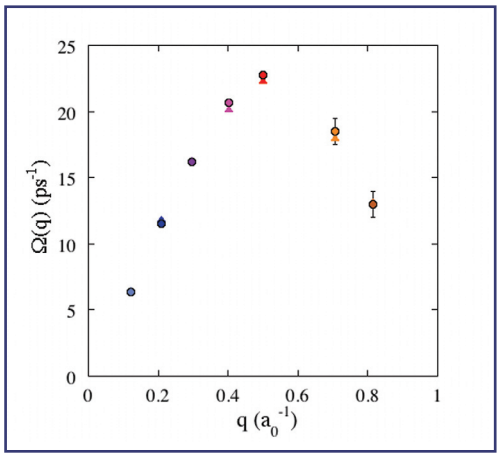


Figure 4—
Comparison between molecular dynamics and V-T theory for one of the cases shown in Fig. 1 at T = 395K.

Figure 5—
Position of the Brillouin peak maximum as a function of q, in the liquid. Molecular dynamics results (circles) and V-T theory (triangles) almost coincide.

For the liquid system, we can still separately evaluate from V-T theory the contribution of only the vibrational motion in one typical single random valley at T = 395K. The comparison with a complete MD evaluation of S(q, ω) is shown in Fig. 4. The striking result is that the position of the Brillouin peak, evaluated from the vibrational motion in a single random valley (V-T theory) and from a MD trajectory that transits among numerous valleys, is the same in both, and we see that the natural width is about half of the width in the liquid. This result is valid for the times, a notion in contrast to previous interpretation.

Work to study the role of transits and how to incorporate them in explicit evaluations within V-T theory is presently underway.

[1] D.C. Wallace, *Phys. Rev. E* **56**, 4179 (1997).

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